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(54) POLYESTER FIBER AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyester fiber having good color tone, scarcely generating spinneret deposits even if continuously spun for a long time through a spinneret, having high performance of good formability, and having improved clearness, and to provide a method for producing the polyester fiber.

SOLUTION: This polyester fiber is produced by the following process: in producing the polyester, a catalyst made from a specific titanium compound and a phosphorus compound is used, and at any stage prior to completing synthesizing the polyester, a metal-containing phosphorus compound and an alkaline earth metal compound are added to the polyester synthesis system without making a reaction between both the compounds in advance, and the resultant polyester polymer obtained by completing the synthesis is melt-spun into fiber, and thereafter, 2-40 wt.% of the resultant fiber is dissolved out by the aid of an aqueous solution of an alkaline compound to form micropores on the cross section of the fiber.

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CLAIMS

[Claim(s)]

[Claim 1] Face manufacturing the fiber which consists ethylene terephthalate of main polyester repeatedly made into a unit, and it is based on all the dicarboxylic acid components from which a meltable titanium compound constitutes polyester in this polyester. As a titanium metallic element, 2-15 millimol % content in the phase of arbitration until the melt spinning of this polyester is completed to the polyester polymer with which it is carried out and is satisfied of the following general formula (1) and (2) The metal-containing phosphorus compounds expressed with the 0.5-1.8-mol % following general formula (I) on the basis of all the acid components that constitute this polyester, It is based on all the acid components that constitute this polyester. A 0.25-3.6-mol % alkaline-earth-metal compound Without making metal-containing phosphorus compounds and alkaline earth metal react beforehand After adding into this polyester composition system, the polyester polymer which was made to complete composition and was obtained The manufacture approach of polyester fiber which the fiber obtained by carrying out melt spinning is made for this 2 - 40% of the weight of fiber to be eluted with the water solution of an alkali compound, and is characterized by making micropore form in a fiber front face.

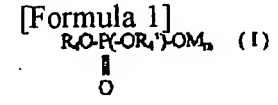
[Equation 1]

$$2 \leq P/Ti \leq 15 \quad (1)$$

$$10 \leq Ti+P \leq 100 \quad (2)$$

(ここで、Tiはポリエステル中に含有されるポリエステル可溶チタン化合物のチタン金属元素の濃度（ミリモル%）、Pはポリエステル中に含有されるリン化合物のリン元素の濃度（ミリモル%）を示す。)

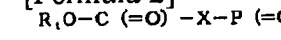
[Formula 1]



(式中、R_4及びR_4'はそれぞれ同一、若しくは異なる一価の有機基、Mはアルカリ金属及び／又はアルカリ土類金属であって、mはMがアルカリ金属の場合には1、アルカリ土類金属の場合は1／2である。)

[Claim 2] The manufacture approach according to claim 1 which adds the phosphonate compound expressed with the following general formula (II) as phosphorus compounds.

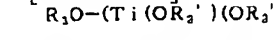
[Formula 2]



(上記式中、R_1及びR_2は、同一又は異なって炭素数原子数1～4のアルキル基を示し、Xは、$-CH_2-$又は$-CH(Y)-$を示す（Yは、ベンゼン環を示す）)

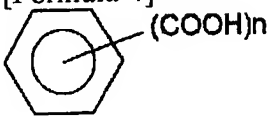
[Claim 3] The manufacture approach according to claim 1 that a titanium compound meltable in polyester is a product to which the aromatic polyvalent carboxylic acid expressed with the compound expressed with the following general formula (III) or the compound expressed with the following general formula (III), and the following general formula (IV) or its anhydride was made to react.

[Formula 3]



(式中、R3，R3'，R3''，R3'''はアルキル基及び又はフェニル基であって、互いに同一であっても異なっていてもどちらでもよい。pは1～3の整数を表す)

[Formula 4]



(IV)

(上記式中、nは2～4の整数を表す)

[Claim 4] The manufacture approach according to claim 3 of adding a part of total addition and/or its whole quantity in the system of reaction before ester exchange reaction initiation, and using a titanium compound meltable in polyester also [catalyst / an ester exchange reaction catalyst and / polycondensation reaction].

[Claim 5] The manufacture approach according to claim 1 that dimethyl terephthalate occupies more than 80mol% among the start source materials of an ethylene terephthalate unit.

[Claim 6] The manufacture approach according to claim 1 of carrying out an ester exchange reaction under the application of pressure of 0.05-0.20MPa.

[Claim 7] Claims 1-6 are polyester fiber obtained by the approach of a publication either.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] the catalyst for polyester manufacture in which this invention contains a specific titanium compound and phosphorus compounds in more detail about polyester fiber and its manufacture approach -- using -- a color tone -- excelling -- a spinneret -- letting it pass -- long duration -- even if it carries out spinning continuously -- a mouthpiece -- it is related with the polyester fiber which has the outstanding engine performance of there being dramatically few yields of an affix and excelling in the moldability and by which clear nature has been improved, and its manufacture approach.
[0002]
[Description of the Prior Art] Since [the] mechanical, physical, and chemical performance are excellent, polyester especially polyethylene terephthalate, polyethylenenaphthalate, polytrimethylene terphthalate, and polytetramethylene terephthalate are widely used for fiber, a film, and other moldingses.
[0003] For example, polyethylene terephthalate is manufactured by carrying out a polycondensation reaction until usually carry out the direct esterification reaction of a terephthalic acid and the ethylene glycol, or it carries out the ester exchange reaction of the low-grade alkyl ester and ethylene glycol of a terephthalic acid like dimethyl terephthalate, or makes a reaction now the ethylene glycol ester of a terephthalic acid, and/or its low-grade polymer generate a terephthalic acid and ethyleneoxide, it subsequently carries out heating under reduced pressure of this resultant under existence of a polymerization catalyst and it becomes predetermined polymerization degree.
[0004] According to the class of catalyst used in these polycondensation reaction phases, it is known well that a reaction rate and the quality of polyester acquired will be influenced greatly. As a polycondensation catalyst of polyethylene terephthalate, an antimony compound has the outstanding polycondensation catalyst engine performance, and it is most widely used from the reasons of the good polyester of a color tone being obtained.
[0005] however -- if melt spinning of the polyester is continuously carried out over long duration when an antimony compound is used as a polycondensation catalyst -- a mouthpiece -- a foreign matter (the following -- only -- a mouthpiece -- a foreign matter may be called) carries out adhesion deposition around a hole, the deflection phenomenon (bending) of melting polymer flow occurs, this becomes a cause and there is a problem of the moldability of generating a fluff, thread breakage, etc. in spinning and a drawing process.
[0006] the case where such a titanium compound is used although using a titanium compound like titanium tetra-butoxide as polycondensation catalysts other than this antimony compound was also proposed -- the above mouthpieces -- although the problem of the moldability resulting from foreign matter deposition is solvable, the obtained polyester itself is colored yellow and the new problem that heat-of-fusion stability is also poor occurs.
[0007] In order to solve the above-mentioned coloring problem, generally adding a cobalt compound in polyester and stopping yellow is performed. Although the color tone (b value) of polyester can improve by surely adding a cobalt compound, by adding a cobalt compound, the heat-of-fusion stability of polyester falls and there is a problem that decomposition of a polymer also becomes easy to take place.

[0008] Moreover, using hydroxylation titanium as other titanium compounds, and using alpha-titanic acid for JP,47-26597,B as a catalyst for polyester manufacture at JP,48-2229,B, respectively is indicated. However, by the former approach, the disintegration of hydroxylation titanium is not easy, since alpha-titanic acid tends to deteriorate by the latter approach on the other hand, the preservation and handling are not easy, therefore neither is suitable to adopt industrially and it is also difficult to obtain the polymer of a still better color tone (b value).
[0009] Moreover, using the product which a titanium compound and phosphite were made to react to JP,58-38722,A again, and was obtained in the product which a titanium compound and trimellitic acid were made to react to JP,59-46258,B, and was obtained as a catalyst for polyester manufacture, respectively is indicated. To be sure, although the heat-of-fusion stability of polyester is improving to some extent according to this approach, the color tone of the polymer obtained is not enough, therefore the further improvement of a polymer color tone is desired.
[0010] Furthermore, in JP,7-138354,A, although making the complex of a titanium compound and phosphorus compounds into the catalyst for polyester manufacture is proposed, and heat-of-fusion stability of a certain extent also improves according to this approach, the color tone of the polymer obtained is not enough.
[0011] In addition, these titanium-Lynn system catalysts were wanted for that catalyst itself to remain as a foreign matter in a polyester polymer in many cases, and to be solved also about this problem.
[0012] Moreover, since [the] mechanical, physical, and chemical performance are excellent, polyester is widely used as a synthetic fiber. However, since there is no depth in a color as compared with wool, a natural fiber like silk, rayon and a semi-synthetic fiber like acetate, and an acrylic fiber when polyester fiber is dyed, it has the fault of being inferior to color enhancement and clear nature.
[0013] In order to improve the dyeing clear nature of this polyester fiber conventionally, an improvement of a color, chemical refining of polyester, etc. are tried and various kinds of proposals are made. For example, by JP,62-44064,B, it is reported by by adding the pentavalent phosphorus compounds of the amount of specification, and the lime compound which is in a specific quantitative ratio to these phosphorus compounds to polyethylene terephthalate that the polyester which was excellent in the depth and clear nature of a color when coloring, and whose discoloration by friction was fully small and was excellent also in fibrillating resistance is obtained.
[0014] Surely, according to this approach, the trouble mentioned above is canceled. since [however,] the chemical refining, therefore the fiber of the fiber using such polyethylene terephthalate itself are soft -- the aforementioned mouthpiece -- it is easy to be influenced by the foreign matter.
[0015] a mouthpiece -- in order to have controlled the foreign matter, it was an effective means not to use antimony as a catalyst as mentioned above, but by the approach which does not use antimony, since the color of yarn fell, an activity was not able to be presented conventionally.
[0016] Therefore, the polyester fiber which did not use antimony as a catalyst, and was excellent in the depth and clear nature of the color tone when coloring and a color, and whose discoloration by friction was fully small and was excellent also in fibrillating resistance was called for.
[0017]
[Problem(s) to be Solved by the Invention] the problem on which the above-mentioned conventional technique had the object of this invention -- solving -- a color tone -- excelling -- a spinneret -- letting it pass -- long duration -- even if it carries out spinning continuously -- a mouthpiece -- it is in offering the polyester fiber which has the outstanding engine performance of there being dramatically few yields of an affix and excelling in the moldability and by which clear nature has been improved, and its manufacture approach.
[0018]
[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating examination wholeheartedly in view of the above-mentioned conventional technique.
[0019] Namely, the object of this invention is faced manufacturing the fiber which consists ethylene terephthalate of main polyester repeatedly made into a unit. It is based on all the dicarboxylic acid components that constitute polyester in this polyester by the meltable titanium compound. As a titanium

metallic element, 2-15 millimol % content in the phase of arbitration until the melt spinning of this polyester is completed to the polyester polymer with which it is carried out and is satisfied of the following general formula (1) and (2) The metal-containing phosphorus compounds expressed with the 0.5-1.8-mol % following general formula (I) on the basis of all the acid components that constitute this polyester, It is based on all the acid components that constitute this polyester. A 0.25-3.6-mol % alkaline-earth-metal compound Without making metal-containing phosphorus compounds and alkaline earth metal react beforehand After adding into this polyester composition system, the polyester polymer which was made to complete composition and was obtained The fiber obtained by carrying out melt spinning is made for this 2 - 40% of the weight of fiber to be eluted with the water solution of an alkali compound, and it can attain by the manufacture approach of polyester fiber characterized by making micropore form in a fiber front face.

[0020]

[Equation 2]

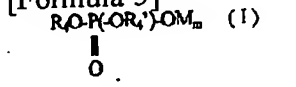
$$2 \leq P/Ti \leq 15 \quad (1)$$

$$10 \leq Ti+P \leq 100 \quad (2)$$

(ここで、Tiはポリエステル中に含有されるポリエステル可溶チタン化合物のチタン金属元素の濃度（ミリモル%）、Pはポリエステル中に含有されるリン化合物のリン元素の濃度（ミリモル%）を示す。)

[0021]

[Formula 5]



〔式中、R_4及びR_4'はそれぞれ同一、若しくは異なる一価の有機基、Mはアルカリ金属及び／又はアルカリ土類金属であって、mはMがアルカリ金属の場合には1、アルカリ土類金属の場合は1／2である。〕

[0022] Furthermore, other objects of this invention are attained by the fiber obtained by the manufacture approach of the polyester fiber of this invention.

[0023]

[Embodiment of the Invention] Hereafter, this invention is further explained to a detail.

[0024] Into a polymer, the polyester of this invention needs to do 2-15 millimol % content of a meltable titanium compound as a titanium metallic element to all dicarboxylic acid components, and needs to satisfy the following general formula (1) and (2).

[0025]

[Equation 3]

$$2 \leq P/Ti \leq 15 \quad (1)$$

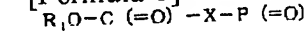
$$10 \leq Ti+P \leq 100 \quad (2)$$

(ここで、Tiはポリエステル中に含有されるポリエステル可溶チタン化合物のチタン金属元素の濃度（ミリモル%）、Pはポリエステル中に含有されるリン化合物のリン元素の濃度（ミリモル%）を示す。)

[0026] In this invention, as phosphorus compounds used, a phosphoric acid, phosphorous acid, phosphonic acid, phosphonate compounds, those derivatives, etc. may be raised, and these may be used independently, and two or more sorts may be used together. The phosphonate compound expressed especially with the following general formula (II) is desirable among these phosphorus compounds.

[0027]

[Formula 6]



〔上記式中、R_1及びR_2は、同一又は異なって炭素数原子数1～4のアルキル基を示し、Xは、$-CH_2-$又は$-CH(Y)-$を示す（Yは、ベンゼン環を示す）〕

[0028] As an above-mentioned phosphonate compound, dimethyl - of phosphonic acid, diethyl -, dipropyl -, and dibutyl ester are mentioned, and KARUBO methoxy methane phosphonic acid, KARUBO ethoxy methane phosphonic acid, KARUBO propoxy methane phosphonic acid, cull

BOPUTOKISHI methane phosphonic acid, a KARUBO methoxy-phosphono-phenylacetic acid, a KARUBO ethoxy-phosphono-phenylacetic acid, a KARUBOPUROTOKISHI-phosphono-phenylacetic acid, a KARUBO butoxy-phosphono-phenylacetic acid, etc. are specifically mentioned.

[0029] The desirable reason of the above-mentioned phosphonate compound is because it has the property which cannot spoil the thermal stability of polyester easily, even when the persistence time under polycondensation reaction also has the long catalytic activity of a titanium compound, and the addition to polyester is made few as a result and it adds an abundant stabilizer to a catalyst like this patent, since it is usually used as a stabilizer and a reaction with a titanium compound advances comparatively gently as compared with phosphorus compounds.

[0030] If the addition stage of these phosphorus compounds is after an ester exchange reaction or an esterification reaction is completed substantially, it is good always, for example, it may add it again after termination of a polycondensation reaction (i.e., after the last stage of a polycondensation reaction under the reduced pressure after starting a polycondensation reaction under the atmospheric pressure before starting a polycondensation reaction also obtains a polymer).

[0031] In this invention, the titanium compound used needs to use a meltable titanium compound in a polymer in respect of foreign matter reduction of a catalyst reason. Although it is not limited but the common titanium compound as a polycondensation catalyst of polyester, for example, acetic-acid titanium, tetra-n-butoxytitanium, etc., is mentioned especially as a titanium compound, especially a desirable thing is the product to which the aromatic polyvalent carboxylic acid expressed with the compound expressed with the following general formula (III) or the compound expressed with a general formula (III), and the following general formula (IV) or its anhydride was made to react.

[0032]

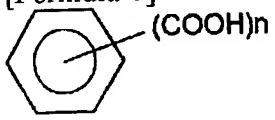
[Formula 7]

$$R_3O-(Ti(OR_3')(OR_3'')_p-OR_3''' \quad \text{(III)}$$

(式中、R3, R3', R3'', R3''' はアルキル基及び又はフェニル基であって、互いに同一であっても異なっていてもどちらでもよい。pは1～3の整数を表す)

[0033]

[Formula 8]



(IV)

(上記式中、nは2～4の整数を表す)

[0034] as the titanium compound expressed with a general formula (III) -- R3, R3', and R3 -- '', R3''' are the same respectively -- or although it differs, and it will not be limited especially if it is an alkyl group and/or a phenyl group, tetraisopropoxy titanium, tetra-propoxytitanium, tetra-n-butoxytitanium, tetra-ethoxy titanium, tetra-phenoxy titanium, OKUTAARUKIRUTORI titanate, hexa ARUKIRUJI titanate, etc. are used preferably.

[0035] Moreover, as the aromatic polyvalent carboxylic acid expressed with the general formula (IV) made to react as this compound, or its anhydride, a phthalic acid, trimellitic acid, a hemi merit acid, pyromellitic acid, and these anhydrides are used preferably.

[0036] What is necessary is to dissolve a part of aromatic polyvalent carboxylic acid or its anhydride in a solvent, to drop a titanium compound at this, and just to make it react for at least 30 minutes at the temperature of 0-200 degrees C, when making the above-mentioned titanium compound, aromatic polyvalent carboxylic acid, or its anhydride react.

[0037] It is necessary to all dicarboxylic acid components to do 2-15 millimol % content of a meltable titanium compound as a titanium metallic element into a polymer at the polyester of this invention. The productivity of polyester falls [this titanium metallic element] under by 2 millimol %, and the polyester of target molecular weight is not obtained.

[0038] Moreover, when this titanium metallic element exceeds 15 millimol %, thermal stability falls to reverse, the molecular weight lowering at the time of fiber manufacture becomes large, and the polyester fiber which was excellent in quality is not obtained. The amount of titanium metallic elements has the desirable range of 2.5 - 12 millimol %, and its range of 3 - 10 millimol % is still more desirable. In addition, "the titanium compound meltable in a polymer" said here shows that the titanium contained in a titanium-dioxide particle is not included, and "the amount of titanium metallic elements" shows the total quantity of the titanium compound used as an ester exchange reaction catalyst, and the titanium compound used as a polycondensation reaction catalyst, when performing the 1st staircase reaction by the ester exchange reaction.

[0039] The polyester in this invention makes a titanium compound a catalyst, phosphorus compounds are manufactured as a stabilizer, and both the following formula (1) and (2) need to satisfy it.

[0040]

[Equation 4]

$$2 \leq P/Ti \leq 15 \quad (1)$$

$$10 \leq Ti+P \leq 100 \quad (2)$$

(ここで、Tiはポリエステル中に含有されるポリエステル可溶チタン化合物のチタン金属元素の濃度（ミリモル%）、Pはポリエステル中に含有されるリン化合物のリン元素の濃度（ミリモル%）を示す。)

[0041] A hue wears yellow remarkably and is not desirable when (P/Ti) is less than two. Moreover, if (P/Ti) exceeds 15, the polymerization reaction nature of polyester cannot fall substantially and cannot obtain target polyester. In the polyester used by this invention, although that it is narrower than the usual metal catalyst characterizes the proper range of (P/Ti), when it is in the proper range, the effectiveness it is ineffective to the former like this invention can be acquired. On the other hand, when (Ti+P) does not fulfill 10, the productivity in a silk manufacture process falls greatly, and the satisfactory engine performance is no longer obtained. Moreover, when (Ti+P) exceeds 100, it generates and is not desirable although the foreign matter resulting from a catalyst is little.

[0042] The range of a formula (1) and (2) is desirable, the range of (Ti+P) in the range of 3-12 and (2) types of (P/Ti) in (1) type is 15-85, and the range of (Ti+P) in the range of 4-10 and (2) types of (P/Ti) in (1) type is 20-70 still more preferably.

[0043] Generally the manufacture approach using the aromatic series dicarboxylic acid represented by the terephthalic acid considering ethylene terephthalate as a raw material of the main polyester repeatedly made into a unit and two approaches using the ester plasticity derivative of the aromatic series dicarboxylic acid represented by dimethyl terephthalate as a raw material are learned.

[0044] The polyester in this invention is the manufacture approach which goes via an ester exchange reaction that dimethyl terephthalate occupies more than 80mol% among the start raw materials of an ethylene terephthalate unit preferably, although there is especially no limit by the manufacture approach. The manufacture approach which uses dimethyl terephthalate for a source material has the advantage that there is little scattering of the phosphorus compounds added as a stabilizer during the polycondensation reaction as compared with the manufacture approach which uses a terephthalic acid as a raw material.

[0045] in addition, within the limits by which the effectiveness of this invention approach is not substantially spoiled by the above-mentioned dimethyl terephthalate -- setting -- concrete -- criteria [molar quantity / acid component sum total] -- carrying out -- less than [10 mol %] -- it is the range not more than 5 mol % preferably, and it and other copolymerizable bifunctional carboxylate may be contained as an additional component.

[0046] The copolymerizable additional component used preferably As an acid component, for example, aliphatic series, such as adipic-acid, sebacic-acid, 1, and 4-cyclohexane dicarboxylic acid, and alicyclic bifunctional dicarboxylic acid, In a list, as more than kinds, such as hydroxycarboxylic acid, for example, a beta-hydroxy ethoxy benzoic acid, and a p-oxy-benzoic acid, and a glycol component A configuration carbon number For example, two or more alkylene glycol, 1, 4-cyclohexane dimethanol, It can choose out of the ester or its anhydride more than neopentyl glycol, bisphenol A, aliphatic series like

Bisphenol S, alicyclic, the diol compound of aromatic series, and a kind of polyoxy-alkylene-glycol **. The above-mentioned additional component may use a kind independently, or may use two or more sorts together. However, copolymerization needs to be within the limits of the above.

[0047] Moreover, the manufacture approach add a part and/or the whole quantity of a titanium compound which can reduce the addition of a titanium compound before ester exchange reaction initiation by the manufacture approach which uses dimethyl terephthalate as a source material, and make the 2 catalysts of an ester exchange reaction catalyst and a polycondensation reaction catalyst use also [approach] is desirable, and the approach which an ester exchange reaction enforces under the application of pressure of 0.05-0.20MPa is more more desirable still.

[0048] In 0.05 or less Mpas, acceleration of the reaction according [the pressure at the time of an ester exchange reaction] to the catalysis of a titanium compound does not have the section enough, on the other hand, by 0.20 or more MPas, the content in the polymer of the diethylene glycol generated as a by-product will increase remarkably, and properties, such as the thermal stability of a polymer, will be inferior.

[0049] In this invention approach, stabilizers, such as trimethyl phosphate, may be added to the system of reaction in the phase of the arbitration in polyester manufacture if needed, and the additive of an antioxidant, an ultraviolet ray absorbent, a flame retarder, a fluorescent brightener, a flatting agent, a ready coloring material, a defoaming agent, and others etc. may be further blended with it.

[0050] Furthermore, in order to tune the color of the polyester obtained finely, the ready coloring material which becomes the system of reaction in the manufacture phase of polyester more than from a kind of organic blue pigments, such as azo, a triphenylmethane color system, quinoline, an anthraquinone system, and a phthalocyanine system, and an inorganic blue pigment can be added. In addition, in the manufacture approach of this invention, it is desirable that cobalt is not substantially included in the polyester which does not need to use the inorganic blue pigment containing the cobalt on which the heat-of-fusion stability of polyester is reduced with a natural thing as a ready coloring material, therefore is obtained.

[0051] 80.0 or more and b value the polyester obtained by this invention approach usually - It is in the range of 2.0-5.0. [L value acquired from a hunter mold color difference meter] Since a whiteness degree becomes it low that L value of polyester is less than 80.0, the high whiteness degree moldings with which practical use can be presented may be unable to be obtained. Moreover, although there is little yellow of this polyester that b value is less than -2.0, since the increase of blueness and the yellow of the polyester which will be obtained if b value exceeds 5.0 on the other hand become strong, manufacture of a practically useful moldings may be unable to be presented. Preferably, 82 or more, L value of the polyester obtained by this invention approach is 83 or more preferably, and is especially range where b value is desirable. - It is 1.0-4.5 and is 0.0-4.0 especially preferably.

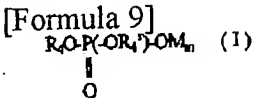
[0052] The polyester of this invention does not contain the cobalt atom originating in the cobalt compound for ready colors substantially. The polyester containing a cobalt atom has the fault that heat-of-fusion stability is low and decomposition becomes easy to take place. In addition, the polyester which does not use a cobalt compound as the ready coloring material "is not included substantially" here, or a polycondensation catalyst, therefore is obtained means that the cobalt atom originating in the above-mentioned cobalt compound is not included. Therefore, the polyester of this invention may contain the cobalt atom originating in the cobalt compound added by having the objects other than a ready coloring material and a catalyst.

[0053] Although what is necessary is just to choose the intrinsic viscosity of the polyester in this invention suitably, it is desirable that it is in the range of 0.55-1.0. If this intrinsic viscosity is within the limits of this, melting shaping will become the easy thing which also has the high reinforcement of a moldings. The still more desirable range of this intrinsic viscosity is 0.60-0.90, and is 0.62-0.80 especially preferably.

[0054] In the manufacture approach of this invention, it is necessary to add further the metal-containing phosphorus compounds shown by the following general formula (I).

[0055]

[Formula 9]



$$R_4O\text{-}P(\text{-}OR_4')\text{-}OM_m \quad (I)$$

$$\begin{matrix} \| \\ O \end{matrix}$$

〔式中、R_4及びR_4'はそれぞれ同一、若しくは異なる一価の有機基、Mはアルカリ金属及び／又はアルカリ土類金属であって、mはMがアルカリ金属の場合には1、アルカリ土類金属の場合は1／2である。〕

[0056] Although R4 and R4' are the organic radicals of monovalence among a formula, here Specifically An alkyl group, an aryl group, an aralkyl radical, or -[(CH2) lO] kR5 However, as for a hydrogen atom, an alkyl group, an aryl group or an aralkyl radical, and l, it is [R5] desirable that the integer of 2-10 and k are integer) of 1-5. (-- M It is desirable to be referred to as Li, Na, K, Mg, calcium, Sr, and Ba, and it is desirable to use especially calcium, Sr, and Ba.

[0057] When the phosphorus compounds by which it replaced with the metal-containing phosphorus compounds of the above-mentioned general formula (I), and R4 and/or R4' were permuted with the metal (especially alkali metal, alkaline earth metal) are used, the micropore generated to the polyester fiber obtained becomes large too much, and the clear-ized effectiveness made into the object is not acquired, and it comes to be inferior also to fibrillating resistance.

[0058] In addition, in order to manufacture this compound, if a solvent carries out the bottom pyrogenetic reaction of existence of corresponding orthophosphoric-acid ester (monochrome, JI, or Tori) and the metallic compounds with which the specified quantity corresponds, it can obtain easily. Furthermore, it is necessary to also use an alkaline-earth-metal compound together with the above-mentioned metal-containing phosphorus compounds, and in the manufacture approach of this invention, as long as it reacts with the above-mentioned metal-containing phosphorus compounds and an insoluble salt is formed in polyester as this alkaline-earth-metal compound, any may be used.

[0059] As this alkaline-earth-metal compound, the acetate of alkaline earth metal, an oxalate, A benzoate, phthalate, organic carboxylate like a stearate, Mineral like a sulfate, a silicate, a carbonate, and a bicarbonate, a halogenide like a chloride, Although alkoxides, such as a chelate compound like ethylenediaminetetraacetic acid complex salt, a hydroxide, an oxide, a methoxide, ethoxide, a phenoxide, and glycoxyde, can be mentioned Especially, it is desirable to use for a trimethylene glycol the organic carboxylate which is fusibility, a halogenide, a chelate compound, and an alkoxide, and especially organic carboxylate is desirable. The above-mentioned alkaline-earth-metal salt may use one sort independently, or may use two or more sorts together, or whichever is sufficient as it.

[0060] When the above-mentioned metal-containing phosphorus compounds and an alkaline-earth-metal compound are used together and alkali loss in quantity of the obtained polyester fiber is carried out, in order to give the depth and its friction endurance of the outstanding color, it is necessary to carry out the amount-used ratio of an alkaline-earth-metal compound to the amount of the metal-containing phosphorus compounds used, and the amount of these phosphorus compounds used as the manufacture approach of this invention.

[0061] Namely, as for the fiber after alkali loss-in-quantity processing, the depth of a color will become inadequate if remainder has few additions of the phosphorus-containing compound used by this invention. although it is alike, and it follows and the depth of a color increases, it becomes difficult to obtain the polyester polymer which makes [many] this amount and which the depth of a color does not show remarkable improvement any longer, but antifriction endurance gets worse on the contrary, and has still more sufficient polymerization degree and softening temperature when it is not much alike and increases itself, and the trouble where thread breakage occurs frequently at the time of spinning occurs. For this reason, the addition of metal-containing phosphorus compounds needs to consider as the 0.5-1.8-mol range of % on the basis of the acid component which constitutes polyester, and is 0.6-1.5-mol % preferably.

[0062] Moreover, on the basis of all the acid components from which the addition of an alkaline-earth-metal compound constitutes polyester, in being fewer than 0.25-mol %, the depth of the color of the polyester fiber obtained is inadequate, it becomes difficult for a polycondensation rate to fall moreover and to obtain high-polymer polyester, and the softening temperature of generation polyester comes to

fall substantially. If 3.6-mol % is exceeded on the basis of all the acid components that constitute polyester, not to mention a big and rough particle will generate inside a polymer and the depth of a color will be improved, visual density falls on the contrary. For this reason, it is necessary to make the addition of an alkaline-earth-metal compound into the 0.25-3.6-mol range of % on the basis of all the acid components that constitute polyester, and it is preferably desirable % and to 0.35-2.2-mol consider as 0.4-1.8-mol % especially.

[0063] Here, in case this alkaline earth metal is added, it is necessary to add in a polyester composition system with the above-mentioned metal-containing phosphorus compounds, without making it react beforehand. An inactive particle can be distributed now in the state of a uniform ultrafine particle in polyester by forming an insoluble salt in polyester within a synthetic system.

[0064] Addition of the above-mentioned metal-containing phosphorus compounds and an alkaline-earth-metal compound can be performed in order of arbitration in the phase of arbitration until composition of polyester is completed, respectively. however, by having added in the phase before reaction termination of a first stage story, only metal-containing phosphorus compounds If the conclusion of the reaction of a first stage story may be checked and only an alkaline-earth-metal compound is added before reaction termination of a first stage story, in making the reaction of this first stage story into an esterification reaction In being easy to generate a big and rough particle during this reaction and considering as an ester exchange reaction Since this ester exchange reaction rate may become large unusually and may cause a bumping phenomenon, when choosing these addition stages, it is desirable to stop to about 20 or less % of the weight on the basis of the total weight of the compound which it is going to add.

[0065] Moreover, it is desirable that the addition stage of metal-containing phosphorus compounds and an alkaline-earth-metal compound adds before the intrinsic viscosity of the reaction mixture in the reaction of a second stage story reaches 0.3 since there is an inclination for the reaction of a second stage story to become inadequate [the phase which advanced to remainder / the depth of condensation of a particle and the color of the polyester fiber obtained eventually that it is easy to produce big and rough-ization].

[0066] Respectively it may add at a stretch, or above-mentioned metal-containing phosphorus compounds and an above-mentioned alkaline-earth-metal compound may be divided into 2 times or more, or may be added continuously.

[0067] In this invention, although the catalyst of arbitration can be used for the reaction of a first stage story In the above-mentioned alkaline-earth-metal compound, what has catalyst ability to the reaction of a first stage story, especially an ester exchange reaction is contained. Although the reaction initiation front stirrup of a first stage story can add using a catalyst independently to ****** when using this compound, and it can add this alkaline-earth-metal compound during a reaction and it can also be made to serve a double purpose as a catalyst Since a bumping phenomenon may be caused as mentioned above, as for the amount used, it is desirable to stop to 20 or less % of the weight on the basis of the total weight of the alkaline-earth-metal compound which it is going to add.

[0068] As explained above, after adding to the polyester system of reaction, without making the above-mentioned metal-containing phosphorus compounds and the above-mentioned alkaline-earth-metal compound of the amount of specification react beforehand, by completing composition of polyester, it has high polymerization, high softening temperature, and good degree [silk manufacture chemically-modified] permeability, and the polyester which can give the fiber which was eventually excellent in both the depth and its friction endurance of a color can be obtained.

[0069] Thus, in order to carry out melt spinning of the obtained polyester and to consider as fiber, even if the fiber which does not need to adopt an exceptional approach, can adopt the melt spinning approach of usual polyester fiber as arbitration, and is spun is solid fiber which does not have a centrum, it may be a hollow fiber which has a centrum. Moreover, the cross-section configuration of fiber and the configuration of a centrum to spin may be a circle type, or may be a variant.

[0070] It faces carrying out spinning furthermore, the polyester which added above-mentioned metal-containing phosphorus compounds and an above-mentioned alkaline-earth-metal compound, and the polyester which is not added are used, and it is good also as a bicomponent fiber of a sheath-core mold,

side by side, and a multilayer laminating mold.
[0071] After performing drawing heat treatment or false twisting from the polyester fiber obtained in this way if needed for removing the part, or after making with a textile, it can carry out easily by carrying out alkali loss-in-quantity processing using the water solution of an alkali compound. Here, as an alkali compound to be used, a sodium hydroxide, a potassium hydroxide, tetraethylammonium hydroxide, a sodium carbonate, potassium carbonate, etc. can be mentioned, and a sodium hydroxide and especially a potassium hydroxide are desirable especially.
[0072] Moreover, although the concentration of the water solution of this alkali compound changes with the class of alkali compound to adopt, processing conditions, etc., it is desirable to usually consider as 0.01 - 40% of the weight of the range, and it is desirable to consider as 0.1 - 30% of the weight of the range especially.
[0073] Furthermore, the processing time is usually performed in for [1 minute] - 4 hours that what is necessary is just to set up this alkali loss-in-quantity processing temperature with about room temperature -100 degree C. Moreover, the amount which carries out elution clearance should be made 2 - 40% of the weight of the range on the basis of fiber weight by processing of the water solution of this alkali compound.
[0074] It comes to present the depth of the color which was excellent when the maximum of frequency distribution was able to make much micropores which have the magnitude which becomes the range whose die length of fiber shaft orientations it is the range whose width of face of the direction of a right angle of a fiber axis is 0.1-0.3 micrometers , and is 0.1-5 micrometers form in a fiber front face and its near by arrange to fiber shaft orientations at parallel and it dyed by perform alkali loss in quantity processing on conditions [**** / conditions] .
[0075]
[Example] Hereafter, although the following example explains this invention concretely further, the range of this invention is not limited by these examples. In addition, about the layer of the affix generated in intrinsic viscosity, a hue, a titanium content, the number of foreign matters, heat-of-fusion stability, and a spinneret, it asked by the approach of the following publication.
[0076] (1) Intrinsic viscosity : the intrinsic viscosity of a polyester polymer was calculated from the value of the viscosity measured in 35 degrees C about the orthochromatic chlorophenol solution.
[0077] Color tone (L value and b value) : (2) Fuse a polymer sample for 10 minutes under 290 degrees C and a vacuum. This is immediately quenched in iced water after fabricating on a plate with a thickness of 3.0**1.0mm on an aluminum plate. this plate -- the white standard plate top for color difference meter adjustment after 160 degrees C and 1-hour desiccation crystallization processing -- placing -- the hunter L value and b value on the front face of a plate -- the Minolta Co., Ltd. make -- it measured using hunter mold color difference meter CR-200. L value shows lightness, it is shown that lightness is so high that the numeric value is large, and it is shown that b value has so large that the value is large the degree of yellow coloring.
[0078] (3) The titanium content of a catalyst : the titanium concentration in a catalyst compound was measured using the Rigaku fluorescence-X-rays measuring device 3270.
[0079] (4) layer [of the affix generated in a spinneret]: -- polyester -- a chip, nothing, and this -- 290 degrees C -- fusing -- aperture 0.15mmphi and a hole -- spinning was carried out for number two days by part for discharge and 600m/from 12 spinnerets, and the height of the layer of the affix generated in the delivery rim of a mouthpiece was measured. Being easy to generate bending in the style of [of the polyester melt breathed out, so that the height of this affix layer was large] the shape of a filament, the moldability of this polyester becomes low. That is, the height of the affix layer generated in a spinneret is the index of the moldability of the polyester concerned.
[0080] (5) Depth of a color : whenever [deep-color] (K/S) was used as a scale which shows the depth of a color. This value measured the spectral reflectance (R) of a sample cloth with the Shimazu RC-330 mold spectrophotometer, and asked for it from the formula of Kubelka-Munk (KubelkaMunk) shown below. It is shown that the bathochromic effect is so large that this value is large.
[0081]

[Equation 5]
$K/S = (1-R)^2/2R$

(式中、Kは吸収計数、Sは散乱計数をそれぞれ示す。)

[0082] (6) Antifriction allochroic : the Gakushin-type flat-surface friction machine for a fastness-to-rubbing trial was used, count flat-surface friction of predetermined of the trial cloth was carried out under the 500g load using the georgette which consists of polyethylene terephthalate 100% as a friction cloth, and extent of generating of discoloration was judged with the gray scale for tenebrescence. The case where abrasion resistance was very low was made into the first class, and the case of being very high was made into the 5th class. The 4th more than class is required practically.
[0083] (7) An elastic modulus, the rate of elastic recovery, reinforcement : it measured using the tension tester ("autograph AG-100E" Shimadzu Corp. make) using the yarn before alkali loss in quantity. It asked for the elastic modulus from the initial inclination of the **** curve obtained from a part for 25-degree-C, trial length [of 25cm], and speed-of-testing/of 20cm. Reinforcement is the same approach and it asked for it as per 1dtex in case yarn fractures being powerful. Moreover, after elongating to 20% of rates of expanding by the above-mentioned approach, the rate of elastic recovery was left for 1 minute, and it asked for it from Itonaga when returning to the die length of a basis at the rate same next again.
[0084] The [example 1] dimethyl terephthalate 194 weight section, the ethylene glycol 124 weight section, and the tetra--n-butyl titanate 0.017 weight section were supplied to the container made from stainless steel in which an application-of-pressure reaction is possible, and the ester exchange reaction was performed in 220 degrees C under the application of pressure of 0.07MPa. As opposed to the acquired resultant Calcium acetate monohydrate of the trimethyl phosphate (it is 0.693-mol % on the basis of all acid components) of the 0.97 sections, and the 0.60 sections (it is based on trimethyl phosphate) 1 / 2 double mol is set in temperature of 120 degrees C in the ethylene glycol of the 16.49 sections. It is the calcium acetate monohydrate (as opposed to trimethyl phosphate) of the bottom of room temperature 1.10 section to the transparence solution 18.06 section of the phosphoric ester calcium salt which was made to react for 60 minutes under [all] a rotary flow, and was obtained. The mixed transparence solution 19.16 section of the phosphoric-acid diester calcium salt and calcium acetate monohydrate which were made to dissolve a mol 1.0 times and were obtained, and the triethyl phosphono acetate 0.08 section were added, and the tera ZORU blue 0.0002 weight section was further added as a ready coloring material.
[0085] After having heated this system of reaction by the temperature of 285 degrees C, and ordinary pressure for 30 minutes, heating under reduced pressure of 4.0kPa(s) (30mmHg) in said temperature for 15 minutes further and advancing a reaction, the inside of the system of reaction was gradually made reduced pressure, it heated for 110 minutes under churning in said temperature, and the reaction was made to complete. The terminal temperature in a flask was 285 degrees C, and the last internal pressure was 49.3Pa (0.37mmHg). The intrinsic viscosity of the obtained polyethylene terephthalate was 0.640. The physical properties of this chip were summarized in a table 1.
[0086] This chip was dried with the conventional method, melt spinning was carried out at 270 degrees C using the spinneret which drilled 36 circular spinning holes of 0.3mm of apertures, subsequently it extended by 3.5 times as many draw magnification as this according to the conventional method, and the raw thread of 75 deniers and 36 filaments was obtained.
[0087] Strong ** of S ** 2500 T/m and Z ** 2500 T/m was given to this raw thread, it was followed, at 80 degrees C, steaming processing was carried out for 30 minutes, this strong throwing was twisted, and the stop was performed.
[0088] It passed through this twist stop strong throwing, S and Z twist were allotted alternately [2] with 47 consistencies/cm and 32 latitude density/cm, and weaving of the crepe georgette textiles was carried out.
[0089] Reflux processing of the obtained gray goods was carried out for 20 minutes by boiling temperature with the rotary washer, crimp **** was performed, it processed in boiling temperature in

3.5% of sodium-hydroxide water solution after presetting with the conventional method, and the textile whose rates of loss in quantity are 10%, 20%, and 30% was obtained.
[0090] It is Dianix about the textile after such alkali treatment. Black Reduction cleaning was carried out for 20 minutes at 70 degrees C with HG-FS(Mitsubishi Chemical Industrial product) 15%owf and the water solution which contains sodium-hydroxide 1 g/L and sodium-hydrosulfite 1 g/L after dyeing for 60 minutes at 130 degrees C, and the black-oxide-finish cloth was obtained. The depth of the color of these black cloths and the antifriction allochroic after 200 wear were shown in the 1st table.
[0091] In the [example 2] example 1, except having changed into the trimellitic acid titanium 0.031 section which compounded the titanium compound by the approach of the example of the following reference, same actuation was performed and polyester and fiber were obtained. A result is shown in a table 1.
[0092] The composition approach of [example [of reference]] trimellitic-acid titanium: 1/2 mol of tetrabutoxytitanium was added to trimellitic anhydride in the ethylene glycol solution (0.2%) of trimellitic anhydride, and you held at 80 degrees C under the ordinary pressure in air, made it react for 60 minutes, cooled in after that and ordinary temperature, made the generation catalyst recrystallize with the acetone of the amount of 10 times, filtered the sludge through the filter paper, it was made to dry at 100 degrees C for 2 hours, and the target compound was obtained.
[0093] Except changing the [examples 1-2 of comparison] titanium compound, and phosphorus compounds into the compound and value which are shown table 1, the polycondensation reaction was performed like the example 1 and polyester and fiber were obtained. A result is shown in a table 1.
[0094] After carrying out an ester exchange reaction to the mixture of the [example 3 of comparison] dimethyl terephthalate 194 weight section, and the ethylene glycol 124 weight section, teaching the tetra--n-butyl titanate 0.017 weight section to the container made from stainless steel in which an application-of-pressure reaction is possible, pressurizing 0.07MPa, and carrying out temperature up to 240 degrees C from 140 degrees C, the triethyl phosphono acetate 0.08 section was added into it, and it was made to end an ester exchange reaction.
[0095] Then, the 3 oxidization 2 antimony 0.101 weight section was added to the resultant, mixture was moved to the polymerization container, temperature up was carried out to 290 degrees C, the polycondensation reaction was performed in the high vacuum of 0.2 or less mmHgs, and the polyester intrinsic viscosity 0.640 and whose amount of diethylene glycols are 1.5 % of the weight was obtained. The obtained polyester fibrosed like the example 1. A result is shown in a table 1.
[0096]
[A table 1]

[0097]
[Effect of the Invention] According to the catalyst of this invention, and the manufacture approach of the polyester fiber using it, even if it excels in a color tone and carries out spinning continuously through a spinneret for a long time, the polyester fiber which has the outstanding engine performance of there being dramatically few yields of opening gilding wear, and excelling in the moldability and by which clear nature has been improved, and its manufacture approach can be offered.